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VARIATIONS IN GLASS MELT BASICITY WITH MAXIMUM INTRODUCTION OF CULLET

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The possibility of increasing the amount of cullet introduced into a glass batch (from 30 to 100%) is demonstrated. A method for evaluation of the variation of the redox potential of the glass melt is proposed using the data on the content of variable-valence iron and sulfur compounds in the glass.

An analysis of the literature data reveals the growing trend for using industrial glass waste, namely, erclese and cullet in the technology of glass production. Maximum possible replacement of the traditional raw materials by cullet makes it possible to bring down the production cost, to utilize glass waste, and to substantially improve the environment at work places. Positive results have mostly been obtained by partly increasing the volume of cullet (above the prescribed values) introduced into a glass batch.

A total replacement of the traditional materials with cullet has been implemented in producing household glass and black marblite slabs [1, 2]. There are data [3, 4] on using the maximum quantity of glass waste in the production of drawn and bulk-tinted rolled glass for architectural and construction purposes. It is notable that the mentioned glass compositions have a lower (0.20 – 0.24%; here and elsewhere weight content, unless otherwise specified) sulfur oxide content than in the traditional technology (over 0.40%) [1 – 4].

Consequently, the technology of producing large volumes of high quality glass melt fully consisting of cullet and converting it into a continuous glass band is in the initial stage of industrial implementation. At the same time, theoretical research on the technological processes involving the maximum possible amount of cullet falls considerably behind the practical implementation. In particular, the data published on decreasing the SO_3 content in industrial cullet-based melts are few. However, the latter circumstance is directly related to the transformation of the valence states of sulfur and iron in glass [5] and, consequently, modification of the stability of the glass-melting process. This aspect of the problem has a practical meaning and merits a detailed investigation.

The purpose of the present study was to investigate the effect of the maximum cullet content in a batch on the modification of the redox equilibrium of iron and sulfur ions contained in the melt in the continuous production of rolled sheet glass. At the same time, an attempt at a comparative estimate of the redox potential (ROP) of melts was made using heterovalent iron and sulfur compounds as the basicity indicators. It is known that iron and sulfur compounds exist in silicate melts in a state of redox equilibrium [5], which depends on the time-temperature conditions of the process, the composition of the gas medium above the melt, the chemical composition of glass, and the ROP of the batch:

$$O_2 + 4Fe^{2+} \leftrightarrow 4Fe^{3+} + 2O^{2-};$$

$$O^{2-} + \frac{1}{2}O_2 + SO_2 = SO_3 + O^{2-} = SO_4^{2-}; \quad (1)$$

$$S^{2-} + 2O_2 = \frac{1}{2}S_2 + \frac{3}{2}O_2 + O^{2-} = SO_4^{2-}. \quad (2)$$

Each of the valence forms of iron and sulfur contained in a melt makes an individual contribution to a modification of the technological properties of the glass melt [5]. The reduced form of iron Fe^{2+}, contrary to the oxidized form Fe^{3+}, decreases the thermal conductivity of a silicate melt. The presence of SO_4^{2-}, which is a product of thermal decomposition of sodium sulfate, on the glass melt surface significantly impairs the homogeneity of glass and leads to its stratification into two liquids non-mixing at high temperatures. Sulfuric anhydride SO_3 is well soluble in a glass melt and simultaneously acts as an oxidizer, a clarifier, and a surfactant. In contrast, sulfurous anhydride SO_2 is not soluble in a glass melt and possesses reducing capacities. It was noted [5] that sulfides, for instance Na_2S, have mostly a positive effect on the glass-melting process.

The combined effect of the above factors determines the formation of a particular ratio of the valence forms of variable-valence elements in the glass melt for each glass-melt-

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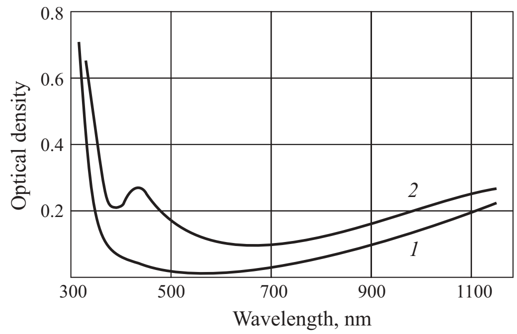

Fig. 1. Spectral curves of optical density of glass samples 1.3 mm thick: *1*) clear glass containing 30% cullet (process 1C); *2*) tinted glass containing 100% cullet (process 1D).

ing furnace. It is possible to estimate the variation in the glass melt basicity based on the variation of the content of valence forms of iron in glass [6].

Manufacturers pay much less attention to the presence of different valence forms of sulfur in a melt than to the presence of iron oxides. However, the information on the variation of the oxidized states of sulfur, in our opinion, can be used as well to develop indicators of the glass melt basicity in a continuous process. Below we present the results of two variants of evaluation of changes in the ROP of glasses using data on the valence transformations of iron and sulfur in melts.

The redox equilibrium of iron and sulfur was analyzed during five technological cycles at different periods of performance of a glass-melting furnace with a daily output of 75 tons of glass melt. The process specifics are indicated in Table 1.

Process 1A involved a batch based on a concentrated material and effective oxidizers. The batch had the highest oxidizing potential among the considered cases, which was determined by calculation [5]. Processes 1B and 1C involved nonconcentrated raw materials. Processes 1A, 1B, and 1C were carried out using the prescribed batch-to-cullet ratio equal to 70 : 30%. An oxidizing medium was maintained inside the furnace. Process 1C is arbitrarily named “the standard process” (for convenience in comparative analysis).

Processes 1D and 1E used industrial glass waste instead of the batch. The glass was melted in a weakly reducing atmosphere. These processes differed from the first three in their higher melting temperature, lower diathermancy, and substantial thermal heterogeneity of the melt.

The ROP of the melts at the first stage was calculated based on the basicity indicator method [6]:

$$d_{\mathrm{Fe(II)}} = \frac{\mathrm{Fe(II)}}{\mathrm{Fe(II)} + \mathrm{Fe(III)}} \times 100, \qquad (3)$$

where $d_{\mathrm{Fe(II)}}$ is the part of bivalent iron in glass, %; Fe(II) and Fe(III) are the weight contents of FeO and Fe_2O_3 on glass converted to metal, %.

Estimation of the ROP based on the above method for clear glass produced in processes 1A, 1B, and 1C does not present difficulties (Table 2). It is more complicated to determine the ROP of tinted glass (process 1D) based only on glass waste.

The spectral curve of this glass (Fig. 1) obtained on a SF-26 spectrophotometer exhibits three clearly expressed transmission bands in the ultraviolet (300 – 350 nm), visible (350 – 540 nm), and infrared (920 – 1100 nm) ranges. The first band is determined by the presence of trivalent iron bonded with oxygen [7]. This compound is arbitrarily designated as Fe(III). The reduced form of iron bonded with oxygen Fe(II) is responsible for the maximum in the long-wave spectrum range [7]. The presence of an intense band with a maximum at 410 nm points to the formation of iron sulfide FeS in tinted glass [5]. Such a band is absent from the optical spectrum of a clear glass of similar composition (Fig. 1 and

TABLE 1

Parameter	Process				
	1A	1B	1C (standard)	1D	1E
Batch components	Concentrated material, cullet, sodium sulfate	Nonconcentrated material, cullet, sodium sulfate	Local material, cullet, sodium sulfate	Polished glass cullet	Cullet (mixture of window and polished glass)
Batch ROP	17.99	16.70	6.80	–	–
Weight content in glass (from analysis), %:					
SiO_2	74.47	74.58	72.89	72.35	72.20
Al_2O_3	0.24	0.15	0.88	1.09	1.55
MeO	8.72	8.79	12.03	12.32	11.39
Na_2O	15.41	15.53	13.70	13.55	14.27
Mean weight content of impurities in glass (from analysis), %:					
Fe_{tot} = Fe(II) + Fe(III)	0.029	0.047	0.083	0.125	0.163
$SO_3 + S^{2-}$	0.560	0.430	0.380	0.270	0.360
Volume content of CO, %	0.0	0.0	0.0	0.2	0.2
Maximum melting temperature, °C	1430	1450	1500	1515	1520
Diathermancy index according to the method in [6]	Not determined	7.5	6.7	5.6	Not determined

Table 1, process 1C). The above data are evidence of the redox reaction between the variable-valence compounds of iron and sulfur in process 1D. At the same time, the decreased diathermancy of the melt and the formation of iron sulfide indicate an increased content of the reduced form of iron and sulfur in glass 1D and, accordingly, a decreased oxidizing potential of the glass melt.

However, the specifics of the calculation of the Fe(II) content indicate that expression (3) takes into account only that part of bivalent iron that is bonded with oxygen. Consequently, for a real estimate of the ROP of glass in process 1D it is necessary to take into account the content of bivalent iron bonded with sulfur sulfide as well:

$$Fe^{2+} + S^{2-} \leftrightarrow FeS.$$

Since the method of combined determination of oxide and sulfide compounds in industrial conditions is not yet developed, the bivalent iron content in the first approximation was determined by analogy with the data in [5] based on optical spectroscopy results (Fig. 1). The following assumptions were made in this case. The total content of iron in glasses produced in processes 1C and 1D is known and determined analytically. The variation of the content of bivalent and trivalent iron, according to the Lambert – Beer law [8]

$$D_\lambda = Kcd,$$

where D_λ is the optical density for the wavelength λ, K is the proportionality coefficient, c is the pigment concentration, and d is the glass thickness, is proportional to the variation of the optical density determined from the spectral curve of the tinted glass (process 1D) for the wavelength typical for each of these compounds (1050, 410, and 380 nm, respectively).

The resulting data are indicated in Table 2. A reference sample for comparison of the spectral properties was the clear glass produced in standard process 1C. It is established that the total content of bivalent iron bonded with oxygen and sulfur in the tinted glass made from cullet (process 1D) is equal to 40.0%. This level is significantly higher than in other glasses produced in processes 1A (19.0%), 1B (25.5%) and 1C (30.1%). In process 1D, 15.2% bivalent iron is bonded with sulfide sulfur and 24.8% is bonded with the oxygen anion. A comparison of the data of processes 1B, 1C, and 1D (Table 2) and the optical transmission spectra (Fig. 1) indicates that FeS is formed under a simultaneous decrease in the content of bivalent and trivalent iron. Table 2 also shows the data on the relative variations in the bivalent iron content in the considered melts compared to the standard process 1C, which correlates with the variation of the glass melt basically.

In the second stage, the variation of the ROP of the melt considered was evaluated using the data on the variation of the valence state of sulfur in the glass melt (reactions (1) and (2)). Significant differences in the physical properties of sulfur compounds [5] were used to develop a second method for the estimation of the oxidation state of the melts.

Since the basicity of glass is proportional to the solubility of SO_3 in a glass melt [5], it was arbitrarily taken that:

– compound $[SO_4]^{2-}$ existing in the melt cannot have a significant effect on the glass basicity, since its content on the glass melt is minimal;

– as the basicity decreases, part of sulfuric anhydride SO_3 passes into the furnace atmosphere in the form of gas SO_2 insoluble in the glass melt according to the reaction:

$$SO_3 \leftrightarrow SO_2 + \frac{1}{2}O_2;$$

– the remaining part of sulfur in the glass melt can be determined analytically and correlates with the total content of SO_3 and S^{2-} dissolved in the glass melt;

TABLE 2

Parameter	Process			
	1A	1B	1C (standard)	1D
Mean weight content of iron in glass, %	0.029	0.047	0.083	0.125
Weight content of bivalent iron, %, bonded with:				
FeO	0.0055	0.0120	0.0250	0.0310
FeS	–	–	–	0.0190
Weight content of trivalent iron, %	0.0235	0.0350	0.0590	0.0760
Part of bivalent iron, %, bonded with:				
FeO	19.0	25.5	30.1	24.8
FeS	–	–	–	15.2
Total part of bivalent iron, %	19.0	25.5	30.1	40.0
Relative variation of:				
part of bivalent iron, %*	33.6	15.2	–	33.0
dissolved SO_3 content** in melts, %	47.3	13.1	–	28.8
100 $\Delta C/C_C$ (mean values)	–	14.1***	–	31.0***

* $\Delta d_{Fe(II)} \times 100/d_{Fe(II)stand}$.

** Based on the absolute value.

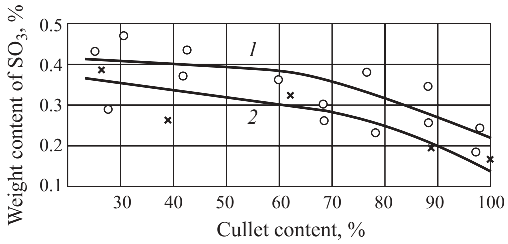

Fig. 2. Effect of increasing cullet content in the batch on the solubility of SO_3 in the glass melt: *1* and *2*) figured and reinforced glass, respectively.

– the variation of the SO_2 content in the gas medium above the melt (ΔC) correlates with the difference between the content of dissolved SO_3 in the melt produced as a consequence of the standard process 1C (C_C) and SiO_3 dissolved in glass in process 1D (C_D):

$$\Delta C = C_C - C_D .$$

Consequently, the relative variation of the content of dissolved SO_3 in the melts

$$100\,\Delta C / C_C \tag{4}$$

in transition from process 1C to process 1D is proportional to the relative variation in the melt basicity.

To understand the specifics of the clarification process, the dynamics of solubility of SO_3 in the melt upon successive replacement of the batch with cullet has practical significance. This dependence is shown in Fig. 2 for figured and reinforced glass. The complete chemical analysis of these glasses was given earlier [4]. It is worth noting that the solubility of SO_3 varies insignificantly, while the cullet content grows from 30 to 70% of the batch, whereas in the interval from 70 to 100% it sharply decreases to $0.24 \pm 0.03\%$. The latter is related to the sulfur equilibrium in the melt shifting toward the lower-valence forms (reactions (1) and (2)) and, in accordance with the above assumptions, points to a relative decrease in the glass melt basicity (expression (4)) by 28.8% compared with process 1C.

The SO_3 content in the melt in reinforced glass molding is significantly lower than in the production of ornamental glass. This is due, in our opinion, to the increased release of gaseous compounds upon contact of the reinforcing metal mesh with the glass melt. The decreased solubility of SO_3 in the cullet-based melts satisfactorily correlates with the data published in the technical literature [1 – 4]. The increased content of dissolved SO_3 in process 1E is related [5] to a higher alkali content than in process 1D (Table 2).

An analysis and a summary of the considered variants of estimating variations in the glass basicity demonstrate that both methods yield mostly a similar general pattern of variation of the ROP of melts. The acidity in process 1D on the whole grows by 31.0% (based on the absolute values of the iron and sulfur indicators) and in process 1B it decreases by 14.1%. The increase in the melt basicity in process 1A using effective oxidizers is significantly higher (33.6% based on the modification of the valence forms of iron, and 47.3% based on sulfur). The spread in the experimental data in process 1A is related to a substantial decrease in the iron content (2.8 times) in glass compared with process 1C.

The results of studying the technological processes on a rolled-glass production line established a decrease in the ROP of the melt (basicity) depending on an increasing quantity of cullet introduced in production. The latter fact together with a weakly reducing atmosphere of the gas medium above the melt produces a shift of the redox equilibrium of iron and sulfur, increasing the content of their reduced forms in the melt. An increased content of bivalent iron oxide determines the decreased diathermancy and impedes the glass-melting process. With an oxygen deficit in the glass melt, part of the sulfur reduced to the sulfide form S^{2-} reacts with bivalent iron and forms the chemical compound FeS, which tints the glass, which is responsible for the emergence of the absorption band at 410 nm in the optical spectrum of the glass melted completely of cullet and gives it its golden-brown tint.

The operation of the rolled-glass production system demonstrated the possibility of producing a continuous glass band and sheet glass for construction purpose based on glass waste of different chemical compositions. In one year of operation of a glass-melting furnace with a daily output of 75 tons of glass melt, substantial material saving was accomplished due to a higher (than the traditional norm) content of cullet in the batch.

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